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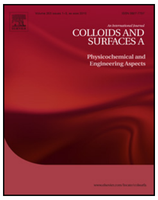

Modelling Eu(III) speciation in a Eu(III)/PAHA/α-Al_2O_3 ternary system

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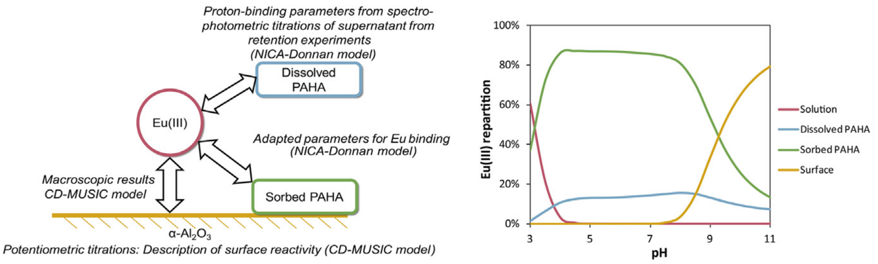
HIGHLIGHTS

- Eu(III) behaviour is described under a various range of environmental conditions.
- CD-MUSIC and NICA-Donnan models are used to calculate Eu(III) speciation.
- Modifications of HA reactivity due to its fractionation are taken into account.
- Model shows that Eu(III) is preferentially bound to adsorbed humic acid fraction.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, modelling of Eu(III) speciation in a ternary system, i.e., in presence of purified Aldrich humic acid (PAHA) and α-Al_2O_3, is presented. First, the mineral surface charge is measured by potentiometric titrations and then described using the CD–MUSIC model. This model is also used to describe Eu(III) binding to the α-Al_2O_3 surface at different pH values, ionic strength and mineral concentrations. Time-resolved luminescence spectroscopy (TRLS) is then used to study the binding of Eu(III) to PAHA at pH 4 with different humic acid concentrations. The spectra are used to calculate a spectroscopic "titration curve", used to determine Eu(III)/PAHA binding parameters in the NICA-Donnan model. Following a previous study (Janot et al., Water Res. 46, 731–740), modelling of the ternary system is based upon the definition of two PAHA pools where one fraction remains in solution and the other is adsorbed onto the mineral surface, with each possessing different proton and metal binding parameters. The modification of protonation behaviour for both fractions is examined using spectrophotometric titrations of the non-adsorbed PAHA fraction at different organic/mineral ratios. These data are then used to describe Eu(III) interactions in the ternary system: Eu(III) repartitioning in the ternary system is calculated for different pH, ionic strength and PAHA concentrations, and results are compared to experimental observations. The model is in good agreement with experimental data, except at high PAHA fractionation rates. Results show that organic complexation dominates over a large pH range, with the predominant species existing as the surface-bound fraction. Above pH 8, Eu(III) seems to be mostly complexed to the mineral surface, which is in agreement with previous spectroscopic observations (Janot et al., Environ. Sci. Technol. 45, 3224–3230).

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1. Introduction

Interactions between humic substances (HS) and mineral surfaces have a great influence on contaminant behaviour in the environment. Presence of humic substances greatly modifies the adsorption of metals onto minerals, and may enhance their solubility and potential transport [1,2]. Several models can describe the different binary systems: Model VI [3] or NICA-Donnan [4] for metal complexation to humic substances, CD-MUSIC for metal adsorption onto surfaces [5,6], Ligand and Charge Distribution (LCD) model for humic substances retention onto oxides [7,8]. However, the additivity of the binary systems - i.e., metal/HS, metal/surface, and HS/surface is often not respected for the ternary systems metal/HS/surface [9,10]. Some studies have succeeded in describing ternary systems containing fulvic acids [11,12], but the larger size and higher heterogeneity of humic acid makes it more difficult to describe [13]. In fact, like real polymers [14], humic acids adsorption onto minerals increases with ionic strength [9,15–17], which is not observed for fulvic acids [18], and is often different from the behaviour of small organic molecules [19]. Recently, Weng et al. [20] succeeded to describe the behaviour of arsenate in a humic acid-containing ternary system; however, arsenate has a different behaviour towards colloids than metallic ions.

Despite numerous studies of these ternary systems, it is still difficult to predict the speciation of metal ions [21,22], a major reason being the fractionation of humic substances constituents when they adsorb onto mineral surfaces [23–27]. This phenomenon has been characterized by several techniques, including UV–visible spectroscopy, size-exclusion chromatography, time-resolved luminescence spectroscopy (TRLS), and asymmetric flow-field flow fractionation. These techniques have been applied to different ternary systems, with contrasting results depending on the mineral surface, the HS origin, and the solution parameters such as pH and ionic strength. The adsorption of HS onto mineral surfaces induces a mass/size fractionation, as noted by several authors [23,24,28,29], but chemical fractionation is also occurring. Spectrophotometric studies show preferential adsorption of the most aromatic moieties [25–27,29]. The two HS fractions – the one in solution and the one onto the surface – present different composition and affinity towards protons and ions [11,26,27].

A new major step to successfully describe a metal/HA/surface system is to characterize the reactivity of HA fractions created upon adsorption. However, this is difficult due to the low concentrations of HA in the supernatant from adsorption experiments. Recently, the use of spectrophotometric titrations has facilitated the measurement of environmentally relevant humic acid concentrations, i.e., less than 10 mg/L [30,31]. In Janot et al. [27], we applied this method to determine the modification of proton-binding behaviour of HA fractions after adsorption onto α-Al_2O_3. Here, Eu(III) speciation is studied in presence of the same purified Aldrich humic acid (PAHA) and α-Al_2O_3 surface. Eu(III) is considered to be (i) a representative of the lanthanides, which use is increasing in modern industry and which are important for understanding geochemical processes; and (ii) as an analogue of some actinides(III). We have already described the evolution of the Eu(III) chemical environment in the binary and ternary systems using time-resolved luminescence spectroscopy (TRLS) [32], which guides our modelling hypotheses. Aluminium oxides are not the most common minerals in the environment, but their surface sites are used here as an analogue of the aluminol surface sites of clays [15], which are ubiquitous in natural systems. Here, we use the CD-MUSIC and NICA-Donnan models to construct a model describing the repartitioning of Eu(III) within the different compartments of the system (solution, surface, adsorbed-PAHA, and dissolved-PAHA).

2. Material and methods

2.1. Materials

The α-Al_2O_3 sample was purchased from Interchim (pure 99.99%, size fraction 200–500 nm). As in previous studies [27,31–33], the solid was washed thrice with carbonate-free NaOH and thrice with milli-Q water before drying and storage at room temperature under N_2(g) atmosphere. Specific area was measured by N_2-BET method and found to be 15 m^2/g.

Europium(III) stock solution (10^{-3} mol/L) was obtained from the dissolution of Eu_2O_3 (Johnson Matthey, 99.99%) in $HClO_4$. All solutions were prepared using freshly boiled milli-Q water.

Commercial Aldrich humic acid was purified (PAHA) according to Kim et al. [34]. Stock suspension at 5 g_{PAHA}/L was prepared by diluting PAHA in NaOH (pH around 10) overnight to completely dissolve the sample.

2.2. Potentiometric titrations of α-Al_2O_3

Potentiometric titrations were performed in a computer-controlled system under N_2(g) atmosphere in a thermostatic vessel (25 °C) equipped with a stirrer using 50 mL solutions at 100 g/L α-Al_2O_3. Ionic strength *I* was fixed using KNO_3 (for 0.01 M and 1 M titrations) or $NaClO_4$ (0.1 M titration). The quoted ionic strengths are the initial values before the addition of any titrant. Experimental values of *I* were calculated for every data point, accounting for both background electrolyte ions and free H^+ and OH^-. The pH values of the solutions were controlled during titrations by addition of 0.1 mol/L acid and base solutions. Base titrant (titrisol for 0.1 mol/L solution) was prepared with degassed Millipore water. The pH values were recorded with two pH Metrohm 6.0133.100 glass electrodes and a single Metrohm 6.0733.100 reference electrode. The pH electrodes were calibrated by performing a blank titration of the background electrolyte prior to the sample titration. The aqueous suspension was purged with N_2(g) at pH 4 for 90 min. The suspension was then titrated by adding small volumes of titrant, and pH was recorded as a function of the titrant volume added to the suspension. After each addition, a drift criterion for pH was used (ΔmV/min < 0.1) and a maximum waiting time of 60 min was set for acquiring each data point. Usually stabilization of pH took less than 2 min. A similar procedure was followed for the blank solution titration. Two forward and backward titrations were performed to eliminate the hysteresis effect.

2.3. Adsorption experiments

The methodology of these experiments have been described in a previous study [33]. Briefly, batch experiments were carried out at ambient temperature with 10^{-6} mol/L Eu(III) concentration at different pH, ionic strengths (0.01 M and 0.1 M $NaClO_4$) and various concentrations of organic and/or inorganic compounds. To minimize carbonation of the systems, and formation of $Eu(CO_3)_n{}^{3-n}$ complexes, headspace was purged with nitrogen prior to closing the tubes. The pH values of the solutions were adjusted by addition of fresh 0.01 or 0.1 mol/L $HClO_4$ or NaOH solutions. They were measured using one combined glass electrode (Radiometer Analytical) connected to a Radiometer Analytical pH Meter. To prevent $KClO_4$ precipitation in the electrode frit, and to minimize junction potential, the electrode filling solution was modified to use 0.1 M NaCl. The pH electrode was calibrated using buffer solutions (pH 4.01, 7.01, and 10.00), yielding σ_{pH} of 0.05–0.08. After 3 days of equilibration, the final pH was checked and samples were ultracentrifuged at 60,000 rpm during 2 h. Eu(III) concentration in the supernatant